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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
25 November 2004 (25.11.2004)

PCT

(10) International Publication Number  
WO 2004/101691 A2

(51) International Patent Classification<sup>7</sup>: C09D 1/00, 7/12, 5/00, 11/02, C08K 3/34, 7/00, D21H 17/68, 19/40

(21) International Application Number: PCT/US2004/013044

(22) International Filing Date: 28 April 2004 (28.04.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 60/467,587 2 May 2003 (02.05.2003) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/101691 A2

(54) Title: PAPER COATING AND FILLER COMPOSITIONS COMPRISING SYNTHETIC PLATY MAGADIITE

(57) Abstract: A coating composition comprising platy magadiite pigment(s); a paper product comprising platy magadiite pigments; and an aqueous suspension comprising platy magadiite and a suspending agent selected from the group consisting of ;polyacrylate polymers, polyvinylalcohol polymers, maleic anhydride-containing copolymers, and polyphosphates, and a latex dispersion or emulsion of latex polymers selected from the group consisting of styrene butadiene polymers, acrylic polymers, carboxylated acrylonitrile :butadiene polymers, polyvinylchloride, polyvinylidenechloride, polystyrene, fluorinated polyethylene and polypropylene, and polytetrafluoroethylene; and an article or formulation comprising a platy layered silicate.

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WO 2004/101691

PCT/US2004/013044

## PAPER COATING AND FILLER COMPOSITIONS COMPRISING SYNTHETIC PLATY MAGADIITE

### Background of the Invention

This invention relates to coating compositions and end-  
5 use applications thereof.

Paper is usually coated to enhance its aesthetic properties. Paper pigments are an integral part of modern paper coating and surface sizing technology. It is well known in the paper industry that a wide variety of pigments, 10 such as titanium dioxide, calcium carbonate, talc, synthetic silicates, and clays such as bentonite and kaolin, are suitable for use as paper fillers and/or coatings. Kaolin, a naturally occurring hydrated aluminate silicate, is presently 15 the most widely utilized and is available in a range of particle sizes and brightnesses.

Surprisingly little use is made by the paper industry of inorganic pigments based on silica or silicates, excluding kaolin clays. Silica and silicates and other pigments, such as  $TiO_2$ , comprise less than 3 percent of the paper pigments. 20 High-structure amorphous silica pigments have been used in the paper industry to replace  $TiO_2$ , at least in part, or to improve ink receptivity. See, for example, G. Alderfer and R. Crawford, Chapter 12—"High Structure Amorphous Silica Pigments in Paper", in *Pigments for Paper*/edited by R. W. 25 Hagemeyer, TAPPI PRESS 1997.

It would be desirable to provide a new class of synthetic paper pigments based on silica or silicates and having a combination of features that are desirable to produce high quality paper products for the printing, food 30 packing, and other industries.

### Summary of the Invention

In a first aspect, the present invention is a coating composition comprising platy magadiite pigment(s).

In a second aspect, the present invention is a coating composition comprising a mixture of platy magadiite pigment(s) with another pigment selected from the group consisting of calcium carbonate, precipitated calcium carbonate (PCC), kaolin, talc, alumina trihydrate, and titanium dioxide.

In a third aspect, the present invention is a paper product comprising platy magadiite pigments.

In a fourth aspect, the present invention is an aqueous suspension comprising platy magadiite and a suspending agent selected from the group consisting of polyacrylate polymers, polyvinyl alcohol, polyphosphates and copolymers of styrene and maleic anhydride resins and other copolymers of maleic anhydride.

In a fifth aspect, the present invention is a suspension comprising platy magadiite, a suspending agent, and a latex polymer or binder selected from the group that includes, for example, styrene-butadiene latex, styrene-acrylate latex, styrene-butadiene-acrylonitrile latex, styrene maleic anhydride latex, styrene-acrylate-maleic anhydride latex, polysaccharides, proteins, polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl acetate, cellulose and cellulose derivatives.

The term "latex polymer" means herein a colloidal dispersion of a polymer in water comprising a cationic, anionic or nonionic polymer dispersed in the aqueous phase and an emulsifying agent.

In a sixth aspect, the present invention is a coating composition comprising layered silicates pigments selected from the group consisting of platy magadiite, platy kenyaite, platy octasilicate, platy  $KHSi_2O_5$ , platy  $Na_2Si_2O_5$  platy talc, platy  $CaCO_3$ , platy bentonite, platy mica, platy satin white, platy vermiculite and other platy pigments.

Other aspects of the present invention will become apparent from the following detailed description and claims.

As used herein, the term "platy magadiite" means a crystalline sodium silicate with a platy morphology comprising substantially flat plates with lateral dimensions [length and width] of from 0.2 to 10 microns, more 5 preferably, from 0.5 to 5 microns and, most preferably, from 1 to 2 microns.

As used herein, the term "layered silicate" means an inorganic material, such as a smectite clay mineral, that is in the form of a plurality of adjacent, bound layers and has 10 a thickness, for each layer, of about 0.03 micron to about 0.5 micron, preferably about 0.1 micron.

Detailed Description of the Invention

Preferably, the platy magadiite employed in the practice of the present invention is a synthetic magadiite comprising 15 more than fifty percent by weight of platy magadiite, more preferably, more than eighty weight percent and, most preferably, more than ninety weight percent by weight of platy magadiite

Platy magadiite can be produced from water glass (water 20 soluble sodium silicate), water and sodium hydroxide (NaOH) under hydrothermal or sub-hydrothermal conditions to yield a crystalline product having platy morphology with crystals resembling flat glass plates of from about 0.2 to about 10 microns in length and from about 0.1 to about 0.1 microns in 25 thickness. The product is produced as a white powder and the platy morphology is ideally suited to produce white and very smooth coatings on paper.

The surface of platy magadiite can be made more or less hydrophilic or hydrophobic by adjustment of the sodium 30 content via titration with inorganic or organic acids and/or by treatment with organic surfactants. These treatments can be used also to tune up the surface acid or basic character. Moreover, it is possible to introduce a variety of functional groups on the platy magadiite surface by reaction of surface 35 silanol (Si-OH) with numerous chemicals to produce functional

surface groups (Si-OR), which may facilitate the interaction of the platy magadiite pigment with the cellulose fiber matrix.

Platy magadiites can be modified with reactive organic 5 coupling agents, such as, for example, organosilanes, alcohols and quaternary salts, to provide paper products with unique surface properties, such as, for example, optical and adhesive properties.

Platy magadiites and their method of preparation are 10 described in detail in copending U.S. Application Serial No. 10/257487, incorporated herein in its entirety by reference.

The platy magadiite pigments of the present invention can be used in a variety of applications such as, for example, nanofiller in polyolefin nanocomposites, paint 15 pigment formulations, catalyst support [Ziegler and Metallocene] for polyolefin catalysts, dye stabilization for use in plastics or in textile fibers containing dispersed dye-magadiite pigment particles and the like.

The platy magadiite pigments can be used also in making 20 (a) paper products comprising platy magadiite in combination with polymer films in bilayer or multilayer articles, b) latex products comprising magadiite in applications other than paper, such as paints and films for road signs, c) cardboard products, d) ink products, e) magadiite-latex 25 additives to FR (flame retardant) formulations, f) magadiite modified with reactive organic coupling agents, such as organosilanes, alcohols, quaternary salts, etc. to provide paper products with unique surface properties, such as, for example, optical and adhesive properties.

30 The platy magadiite pigments can be used also in combination with binders, such as latex, starch and co-binders such as carboxy methyl cellulose (CMC) and other additives, including lubricants and surfactants, rheology modifiers and dispersing agents used to make paper coatings.

The platy magadiite pigments can be used also in the paper making process as a filler.

In general, the paper coating composition of the present invention can be prepared by dispersing the magadiite pigment 5 in deionized water.

The amount of platy magadiite pigment used depends on the desired paper coating performance including sheet gloss, ink gloss, brightness, opacity, Helio, roughness, CIE whiteness, B-value, and the like; the relative amounts of 10 other pigments such as calcium carbonate, kaolin, titanium dioxide; and the relative amounts of other components such as latex, surfactants and dispersing agents.

In general, the platy magadiite pigment is used in an amount of from about 0.1 wt. percent to about 30 wt. percent, 15 more preferably, from about 1 wt. percent to about 30 wt. percent and, most preferably, from about 3 wt. percent to about 30 wt. percent, based on the weight of the paper composition comprising base paper or raw stock, paper pigment, and binder.

20 Advantageously, the platy magadiite pigments are suspended in water using suspending agents to disperse and stabilize the platy particles at concentrations and viscosities suitable for application as coatings on paper.

The suspending agents which can be employed in the 25 practice of the present invention include, for example, polyacrylate polymers, such as, for example, DISPEX™ N40, a salt of a polymeric acid in aqueous solution, a product of Allied Colloids Inc., polyvinyl alcohol, such as, Polyvinyl Alcohol 103, a product of Air Products, polyphosphates, such 30 as potassium tripolyphosphate, sodium hexametaphosphate, tetrasodium pyrophosphate, and copolymers of styrene and maleic anhydride resins and other copolymers of maleic anhydride.

The preferred suspending agents are polyvinyl alcohol, polyacrylate and maleic anhydride-containing copolymer resins, and polyphosphates. The more preferred suspending agents are polyvinyl alcohols, polyacrylate and polyacrylate copolymers. The most preferred suspending agents are 5 Polyvinyl Alcohol 103 and Dispex™ N40.

The amount of suspending agent employed in the practice of the present invention depends on the desired solids content in the pigment dispersion and on the solids 10 composition. In general, the suspending agent is used in an amount of from about 0.01 wt. percent to about 2.0 wt. percent, more preferably, from about 0.05 wt. percent to about 1.0 wt. percent and, most preferably, from about 0.05 wt. percent to about 0.5 wt. percent, based on the weight of 15 the pigment in the composition.

Preferred latex polymer dispersions or binders which can be employed in the practice of the present invention include, for example, carboxylated styrene-butadiene latex, carboxylated styrene-acrylate latex, carboxylated styrene-butadiene-acrylonitrile latex, polyvinyl alcohol, and carboxylated copolymers of polyvinyl acetate and acrylate ester latex.

Polysaccharides which can be employed in the practice of the present invention include, for example, agar, sodium 25 alginate and starch including modified starches such as thermally modified starch, carboxymethylated starch, hydroxyethylated starch and oxidized starch.

Examples of proteins that can be suitably used in the practice of the present invention include albumin, soy 30 protein and casein.

The magadiite pigment of the present invention can be used in a variety of other applications such as, for example, nanofiller in polyolefin nanocomposites, paint pigment formulations, catalyst support [Ziegler and Metallocene] for 35 polyolefin catalysts, dye stabilization for use in plastics

or in textile fibers containing dispersed dye-magadiite pigment particles and the like.

The following working examples are given to illustrate 5 the invention and should not be construed as limiting its scope. Unless otherwise indicated, all parts and percentages are by weight.

The terms used in the Examples are defined as follows:

10	DISPEX™-N40	Salt of a polymeric acid in aqueous solution, a product of Allied Colloids Inc.
15	Cowl™ Mixer	A high shear mixing system used to disperse the pigment and produce a stable slurry. This device is made by Morehouse Industries, Inc.
20	CP 638NA	Carboxylated styrene/butadiene latex, a product of The Dow Chemical Company.
25	FINNFIIX® 10	Carboxy methylcellulose, a rheology modifier. FINNFIIX 10 is a registered trademark of Metsaeleton.
30	RAP™ 501NA	Carboxylated Styrene/butadiene/acrylonitrile latex, a product of The Dow Chemical Company.
35	Roto base paper	A paper that is coated with a pigment and binder package that is suitable to be printed using the Roto Gravure printing process.
	Dow Bench Blade coater	A table bench scale coater to apply the paper coating formulation to the paper and uses a blade to doctor the excess coating to produce a smooth coated surface.

EXAMPLE 1 Roto Gravure Coating Formulation

1) Pigment Dispersion

The pigment was dispersed in deionized water at 43 40 percent solids using 0.25 parts of a dispersant, Dispex-N40,

based on 100 parts dry pigment. The dispersant was added to the water and then the platy magadiite pigment was slowly added while mixing with a Cowl Mixer. The agitation rate was increased when all the platy magadiite pigment is added to 5 the water, and the platy magadiite pigment was left to mix for 15 minutes.

2) Paper Coating Formulation

Several paper coating formulations were prepared by mixing the different components for each coating formulation 10 in the order that they appear in Table 1. The rheology modifier, carboxy methylcellulose (Finnfix 10) was added to provide some thickening to achieve the required coat weights. The formulations were prepared at 51 percent solids and the pH was adjusted with NaOH to 8.5.

15 3) Preparation of Samples

The paper coating formulation was applied using the Dow Bench Blade coater. The coatings were applied on a wood containing Roto base paper. The target coat weight was 4.5-lbs/3300 sq. ft.

20 The coated paper samples were then supercalendered using a standard lab scale super calender. The control, which is formulation 1, was calendered to target gloss at 1500 pounds per lineal foot (pli) and 67°C. The same super calender conditions were then used for all other coating systems.

25 The paper samples were then left to condition to constant moisture condition before testing. The samples were then tested for key properties including optical and print performance. The results are shown in Figures 1-8.

30 Test Procedures

1. Sheet Gloss TAPPI Test Method - T480
2. Ink Gloss<sup>A</sup>
3. Brightness TAPPI Test Method - T646

4.	Opacity	TAPPI Test Method - T425
5.	Helio <sup>B</sup>	
6.	Roughness	TAPPI Test Method - T555
7.	Whitenesss	TAPPI Test Method - T-560
5	8. CIE B-Value	TAPPI Test Method - T-560
	9. Coated Paper Strength	TAPPI Test Method - T514

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<sup>A</sup>Ink Gloss Test Procedure

10 A thin ink film is applied to a strip of paper using a Prufbau Printability tester and then the ink is allowed to dry at room temperature. The printed samples are then measured for ink gloss (Print Gloss) using the same procedure as in T480. The only difference is the application of the ink film using the Prufbau. The Prufbau Printability Tester is a product of Prufbau Company in Germany.

<sup>B</sup>An Helio Test Procedure

20 An ink film is applied using a Reprotest I.G.T. ACII 5 Printability Tester product of IGT, and Heliotest Kit.

25 The ink is applied to the paper using an engraved wheel following the procedure described below. When the ink is transferred from the engraving of the wheel to the paper, sometimes ink does not transfer from some of the cells or engravings. This will result in a missed ink dot on the printed paper. This phenomenon is referred to as a missing dot. The number of missing dots in a 20 mm length of a printed strip of paper is used as a measure to quantify the quality of the Roto print. The higher the number of the missing dots, the lower the print quality. An optimal number is 0 missing dots.

Procedure:

30 1. Replace cardboard backing on IGT with green rubber backing and Mylar Film from Heliotest kit.

35 2. Place support-holder plate into upper IGT slot. Attach beveled blade to weight arm and slide onto plate. Adjust plate so that the blade rests aligned on the Heliotest wheel and tighten (plate should be approximately vertical).

3. Switch IGT to constant speed and set speed to 1.0 m/s remember to use constant speed scale.

4. Start with pressure (upper hub) of 50 kilogram force (kgf).

40 5. Place 2 to 3 drops Heliotest ink onto engraved wheel with measuring scale and spin wheel clock-wise. Only engraved depressions should appear tinted against the shine of the chrome. (Heliotest ink is prepared by cutting gravure printing ink with N-butyl carbitol acetate to 75 cP brookfield or 23 seconds with #4 Shell cup.) If streaking occurs, clean wheel and IGT's beveled blade. Re-ink as needed to keep even distribution in the depressions of the wheel.

45 6. Stop wheel with the blade resting within 1 inch of the end of the wide band.

7. Run a strip (strips need only be attached by the lead clip).

8. Count missing dots in the inked band on strip from dark to light. Mark strip at 20 missing dots. This should fall approximately 60 to 70 for the control then the rest of the samples are run at that condition. If it is out of this range, adjust pressure until it is reasonably close. (Raising pressure should raise the 20-dot mark).

5 9. Run samples randomly. Measure distance in mm to the mark. The greater distance to 20 missing dots, the better the printability.

10 10. Clean up with acetone.

15

Table 1: Paper Coating Formulation  
Total of 100 Parts Including Plastic Pigment

Formulations 1-10

PIGMENTS	1*	2	3	4*	5	6	7*	8	9*	10
Hydraphint	100	85	75	100	85	75				
Hydrocarb 90							100	75	100	75
Magadiite		15	25		15	25		25		25
<b>BINDERS/ADDITIVES</b>										
Dry Parts per 100 parts Pigment										
Rap 501	6	6	6				6	6		
CP 638				6	6	6			6	6
Finnfix 10	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
<b>Aim Points:</b>										
% Solids	51%	51%	51%	51%	51%	51%	51%	51%	51%	51%

\*control

20

Figures 1-9 show that the use of Magadiite pigment in any formulation and with any latex resulted in:

- 1) Better gloss and printed ink gloss.
- 5 2) Better brightness with pigment systems; clay and carbonate. However more brightness improvement with the carbonate formulation.
- 3) Better opacity with both pigment systems and with both latexes.
- 10 4) Better Whiteness and more blue coating with both with all the different systems.
- 5) Far better Hellio, which is a measure of Gravure, print quality. This improvement was evident across all the systems.
- 15 6) Offset latex like CP 638NA demonstrated improved Roto prints performance in the presence of platy magadiite-based pigment. This could not be done with traditional pigment systems.
- 7) The coated paper surface with platy magadiite appears to have a higher binder demand as shown by Figure 9. This suggest that coating made with platy magadiite will require slightly more binder especially for the offset printing process.

Although the invention is specifically described with respect to the preferred embodiment, that is, platy magadiite, the present invention also encompasses other platy layered silicates, such as platy octasilicate, platy kenyaite and related materials such as platy  $KHSi_2O_5$ , and platy  $Na_2Si_2O_5$ . These platy layered silicates typically have a platy morphology comprising substantially flat plates which are from 0.5 to 10 microns long, and from 0.01 to 0.1 microns thick, or have aspect ratios of from 5 to 1000.

WHAT IS CLAIMED IS:

1. A coating composition comprising platy layered silicate pigment(s).
2. The coating composition of Claim 1 wherein the layered silicate pigment(s) is present in an amount of from 0.1 wt. percent to 30 wt. percent, based on the weight of the composition.
3. The coating composition of Claim 1 wherein the platy layered silicate is a synthetic magadiite comprising more than fifty percent by weight of platy magadiite.
4. The coating composition of Claim 1 wherein the platy magadiite is a synthetic magadiite comprising more than eighty percent by weight of platy magadiite.
5. The coating composition of Claim 1 wherein the platy magadiite is a synthetic magadiite comprising more than ninety percent by weight of platy magadiite.
6. The coating composition of Claim 1 wherein the platy layered silicate is selected from the group consisting of platy magadiite, platy kenyrite, platy octasilicate, platy  $KHSi_2O_5$ , and platy  $Na_2Si_2O_5$ .
7. The coating composition of Claim 1 further comprising another pigment selected from the group consisting of calcium carbonate, precipitated calcium carbonate (PCC), kaolin, talc, alumina trihydrate, titanium dioxide, platy talc, platy  $CaCO_3$ , platy bentonite, platy mica, platy satin white and platy vermiculite.
8. The coating composition of Claim 3 wherein the platy magadiite is modified with a reactive coupling agent selected from the group consisting of organosilanes, alcohols and quaternary salts.
9. A paper product comprising platy layered silicate pigments.

10. The paper product of Claim 9 wherein the platy layered silicate is a synthetic magadiite comprising more than fifty percent by weight of platy magadiite.

11. The paper product of Claim 9 wherein the platy 5 layered silicate is a synthetic magadiite comprising more than fifty percent by weight of platy magadiite.

12. The paper product of Claim 8 wherein the platy layered silicate is selected from the group consisting of platy magadiite, platy kenyait, platy octasilicate, platy 10  $\text{KHSi}_2\text{O}_5$ , and platy  $\text{Na}_2\text{Si}_2\text{O}_5$ .

13. A latex product comprising platy layered silicate pigments.

14. The latex product of Claim 13 wherein the platy layered silicate is a synthetic magadiite comprising more 15 than fifty percent by weight of platy magadiite.

15. A cardboard product comprising platy layered silicate pigments.

16. Paints or films for road signs comprising platy layered silicate pigments.

20 17. Ink products comprising platy layered silicate pigments.

18. A flame retardant composition comprising platy layered silicate pigments.

19. An aqueous suspension comprising a platy layered 25 silicate, a suspending agent and a latex polymer.

20. The aqueous suspension of Claim 19 wherein the suspending agent is selected from the group consisting of polyacrylate polymers, polyvinylalcohol polymers, maleic anhydride-containing copolymers, and polyphosphates maleic 30 anhydride-containing copolymers, and polyphosphates

21. The aqueous suspension of Claim 19 wherein the platy layered silicate is a synthetic magadiite comprising more than fifty percent by weight of platy magadiite.

22. The aqueous suspension of Claim 19 wherein the platy layered silicate is a synthetic magadiite comprising more than eighty percent by weight of platy magadiite.

23. The aqueous suspension of Claim 19 wherein the 5 platy layered silicate is a synthetic magadiite comprising more than ninety percent by weight of platy magadiite.

24. The aqueous suspension of Claim 19 wherein the platy layered silicate is selected from the group consisting of platy magadiite, platy kenyaita, platy octasilicate, platy 10  $\text{KHSi}_2\text{O}_5$ , and platy  $\text{Na}_2\text{Si}_2\text{O}_5$ .

25. The aqueous suspension of Claim 20 wherein the latex polymer is selected from the group consisting of styrene-butadiene latex, styrene acrylate latex, styrene-butadiene-acrylonitrile latex, styrene maleic anhydride 15 latex, styrene-acrylate-maleic anhydride latex,

26. The aqueous suspension of Claim 25 wherein the latex polymer is selected from the group consisting of carboxylated styrene-butadiene latex, carboxylated styrene-acrylate latex, carboxylated styrene-butadiene-acrylonitrile 20 latex, polyvinyl alcohol, and carboxylated copolymers of polyvinyl acetate and acrylate ester latex.

27. An aqueous suspension comprising a platy layered silicate, a suspending agent, and a binder selected from the group consisting of starch, cellulose and protein.

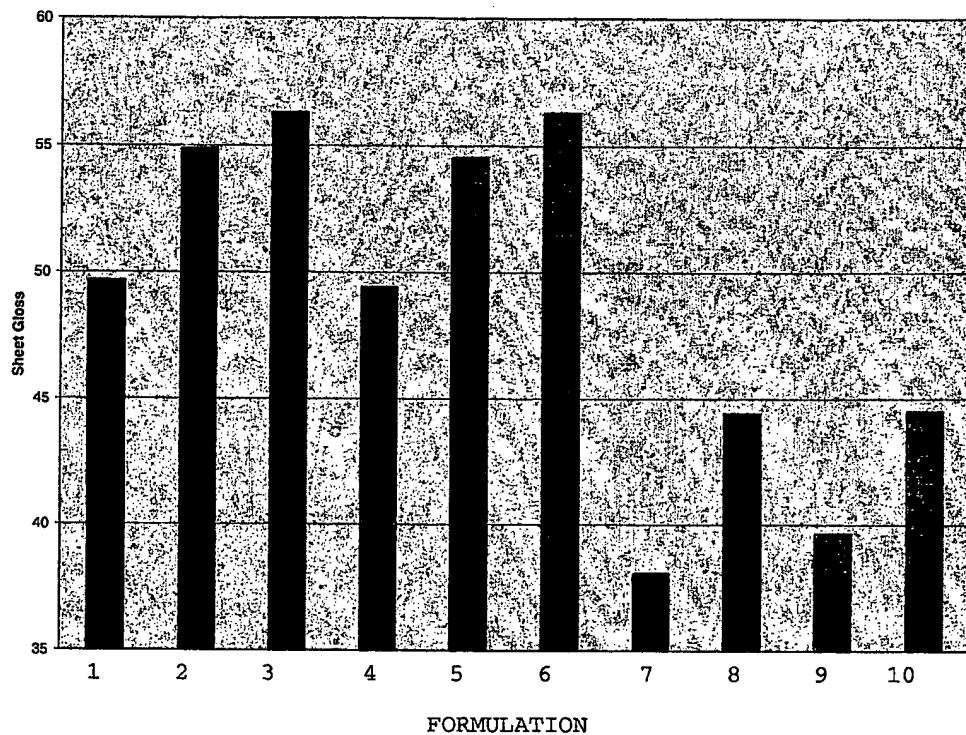
28. An article or formulation selected from the group 25 consisting of (1) a nanofiller in polyolefin nanocomposites, (2) a paint pigment formulation, and (3) a catalyst support for polyolefin catalysts, each comprising a platy layered silicate.

29. The article of Claim 28 wherein the platy layered silicate is a synthetic magadiite comprising more than fifty 30 percent by weight of platy magadiite.

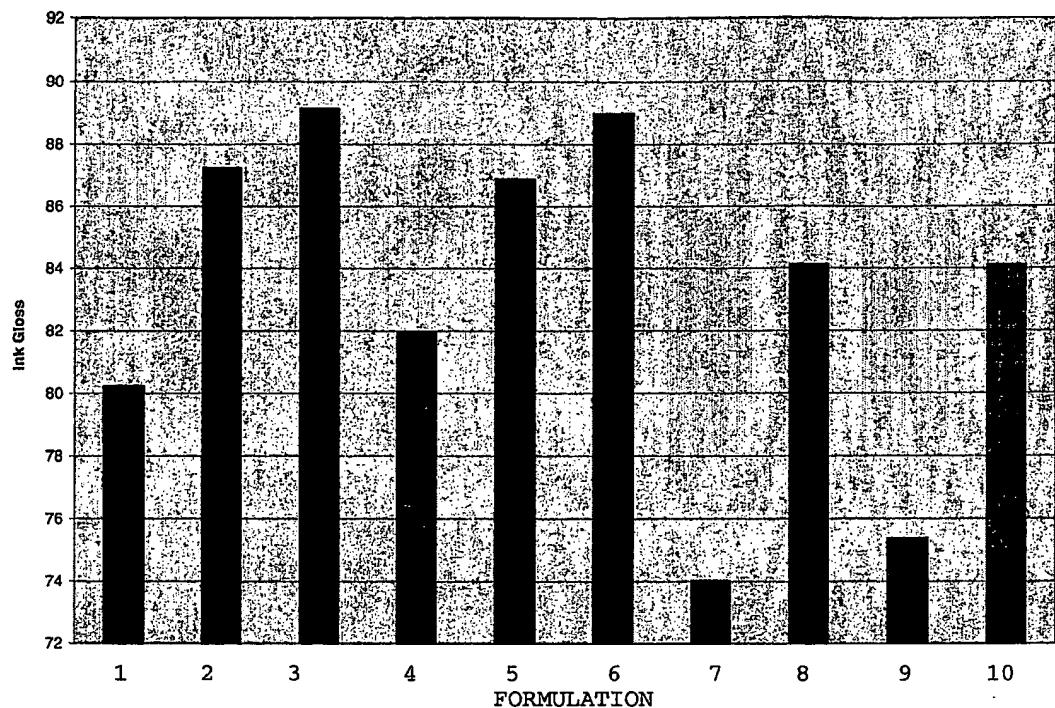
30. The article of Claim 28 wherein the platy layered silicate is selected from the group consisting of platy

magadiite, platy kenyaite, platy octasilicate, platy  $\text{KHSi}_2\text{O}_5$ , and platy  $\text{Na}_2\text{Si}_2\text{O}_5$ .

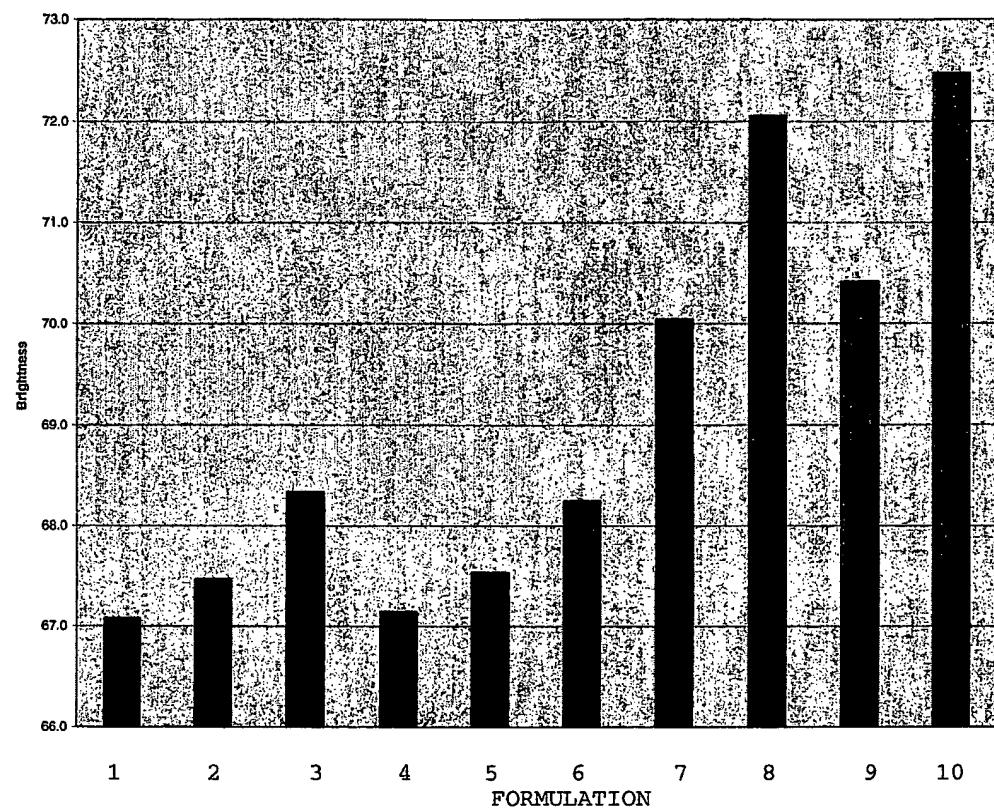
1 / 9

**Figure 1: Sheet Gloss**

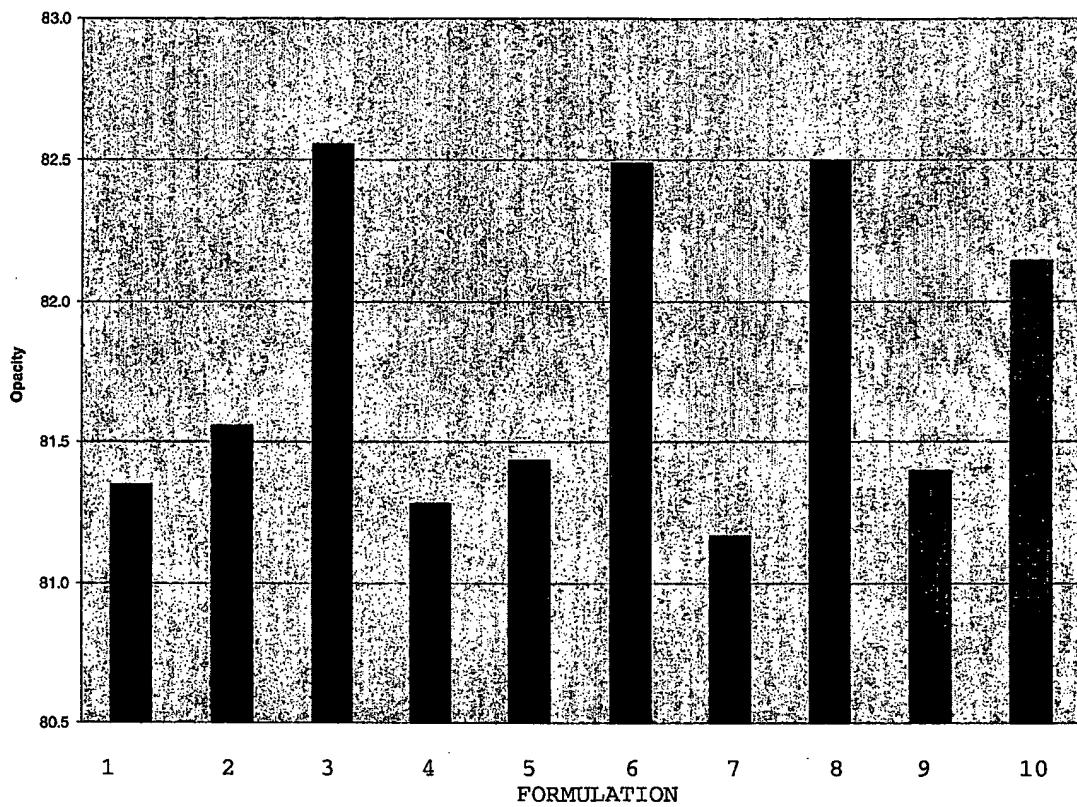
**Figure 2: Ink Gloss**



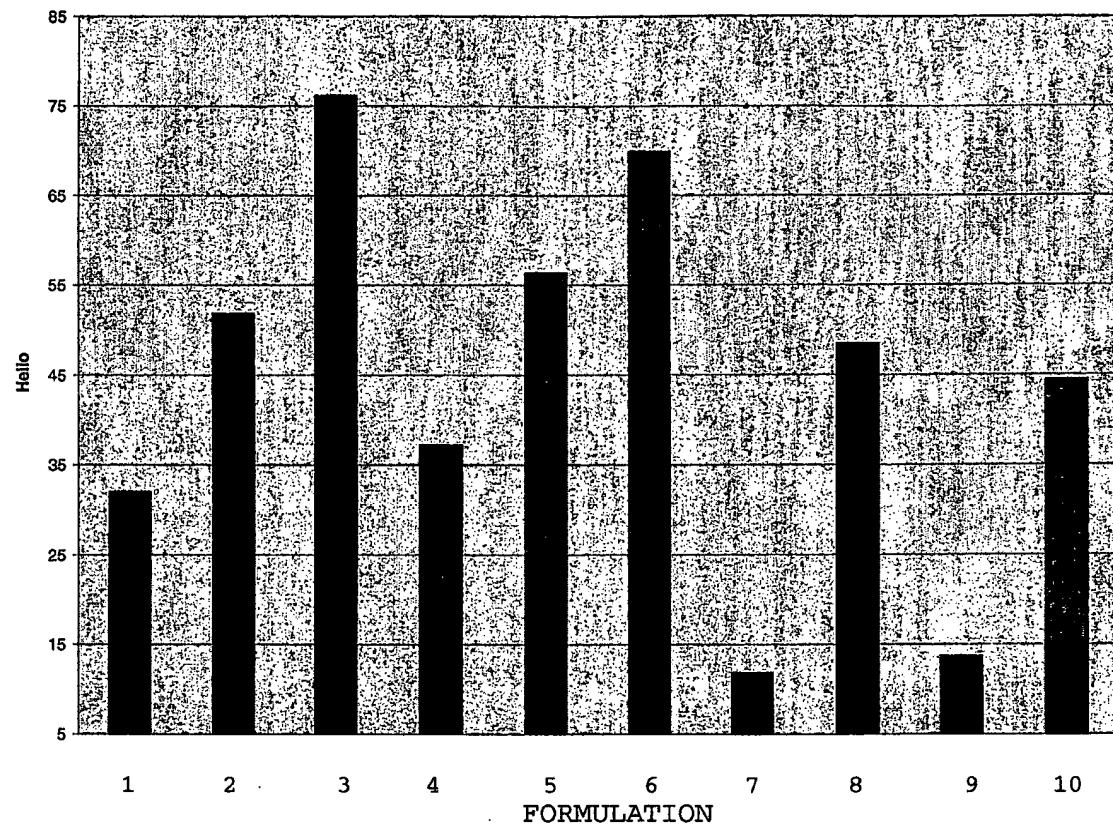
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**Figure 3: Brightness**

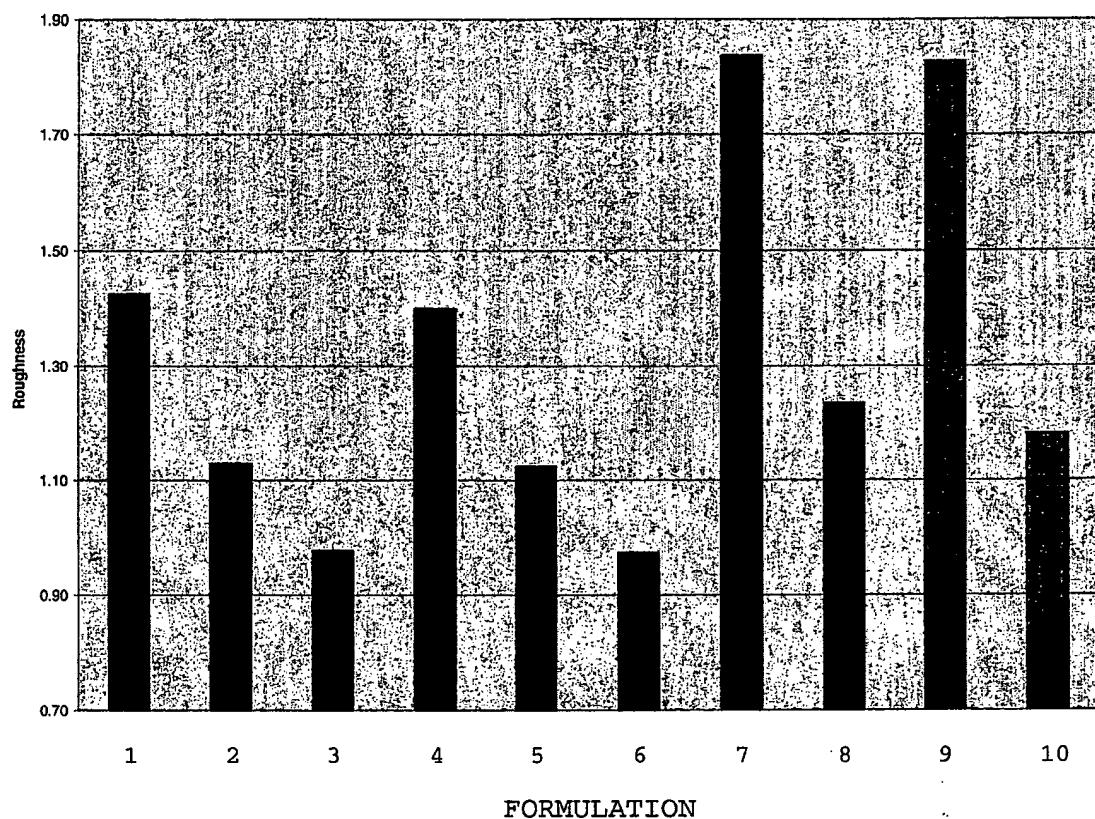
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**Figure 4: Opacity**

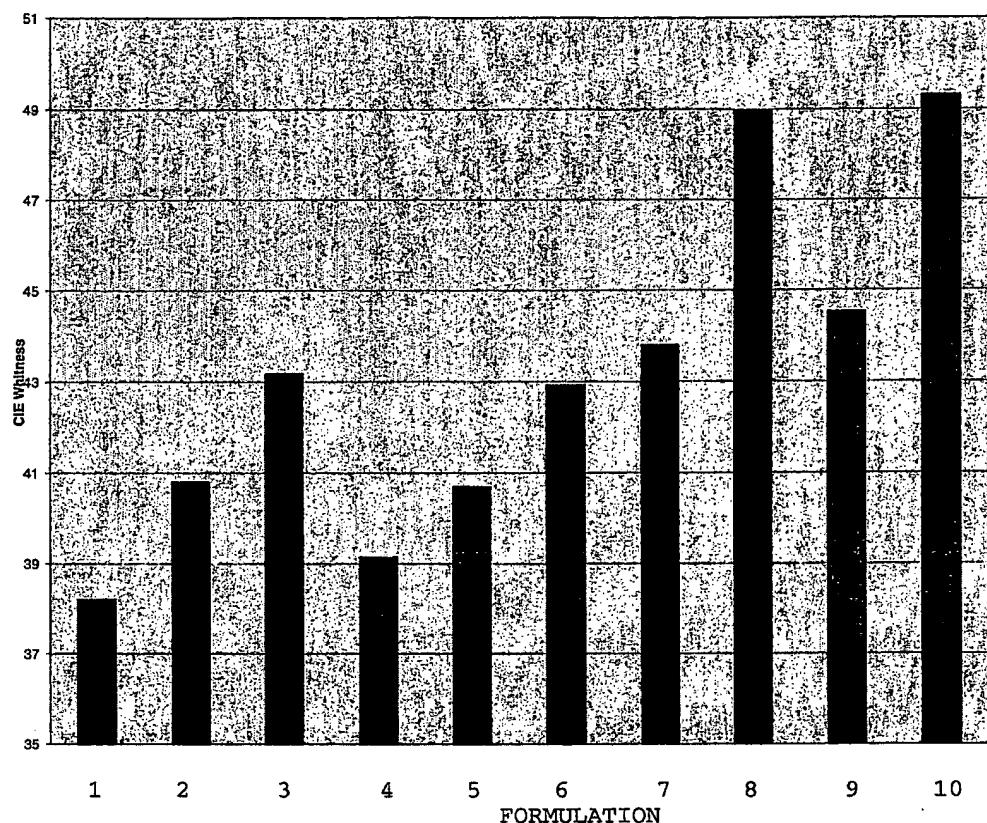
5 / 9

**Figure 5: Helio (Distance in CM to Missing Dots)**

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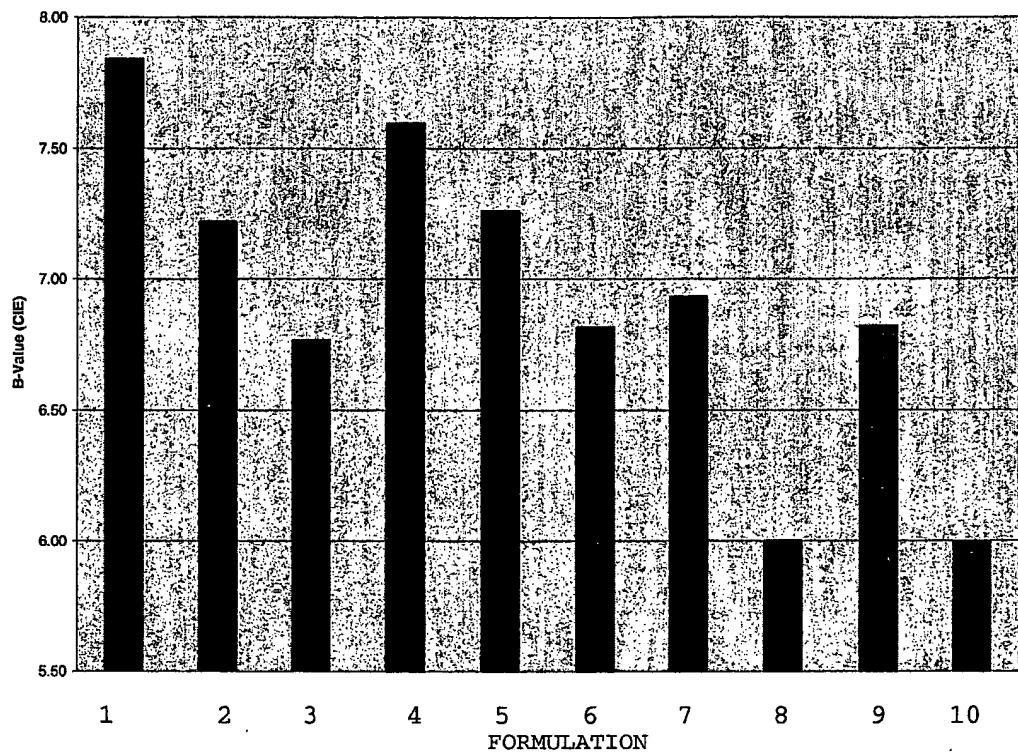
**Figure 6: Coated Surfaces Roughness (microns)**

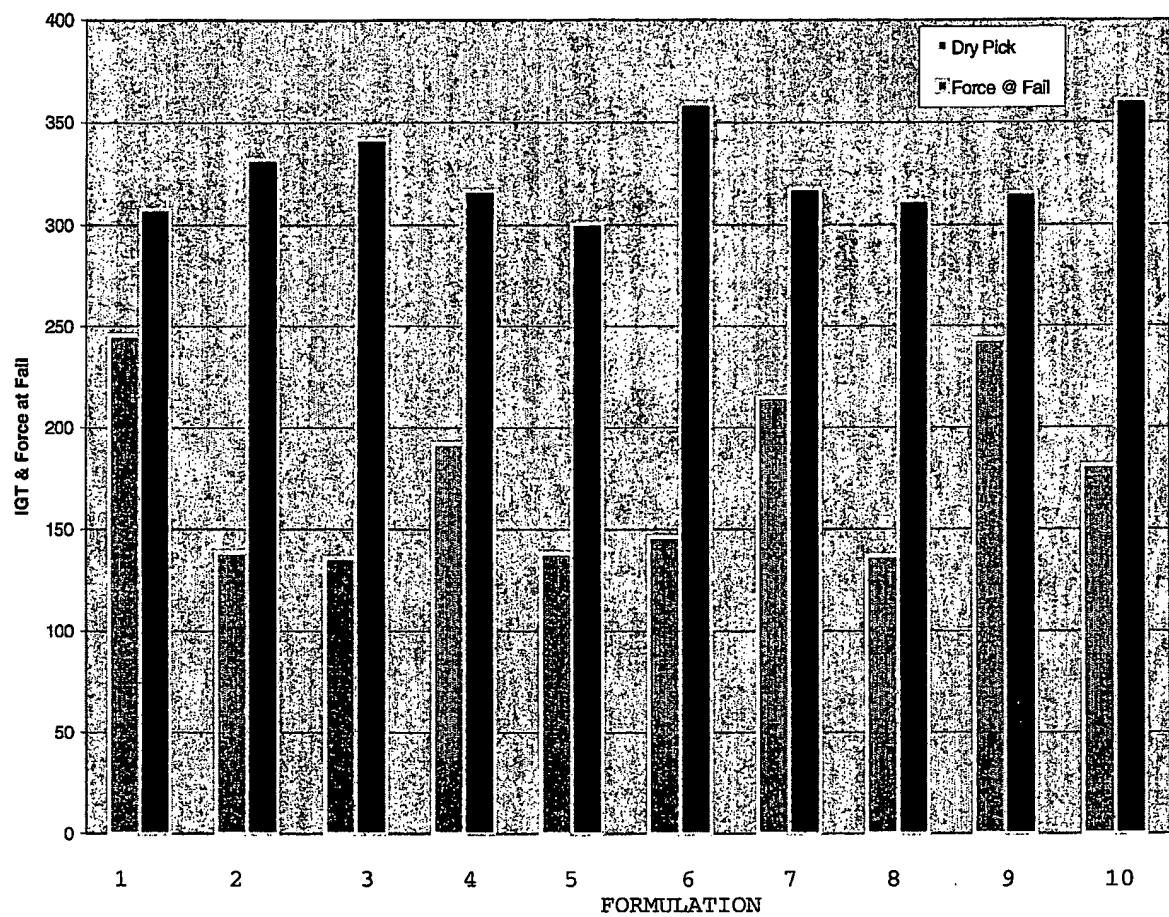
7 / 9

**Figure 7: Whiteness**

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**Figure 8: CIE B-Value (Lower More Blue)**



**Figure 9: Coated Paper Strength**

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date  
25 November 2004 (25.11.2004)

PCT

(10) International Publication Number  
**WO 2004/101691 A3**

(51) International Patent Classification?: C09C 1/00, C09D 7/12, 5/00, 11/02, C08K 3/34, 7/00, D21H 17/68, 19/40

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(21) International Application Number:

PCT/US2004/013044

(22) International Filing Date: 28 April 2004 (28.04.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/467,587 2 May 2003 (02.05.2003) US

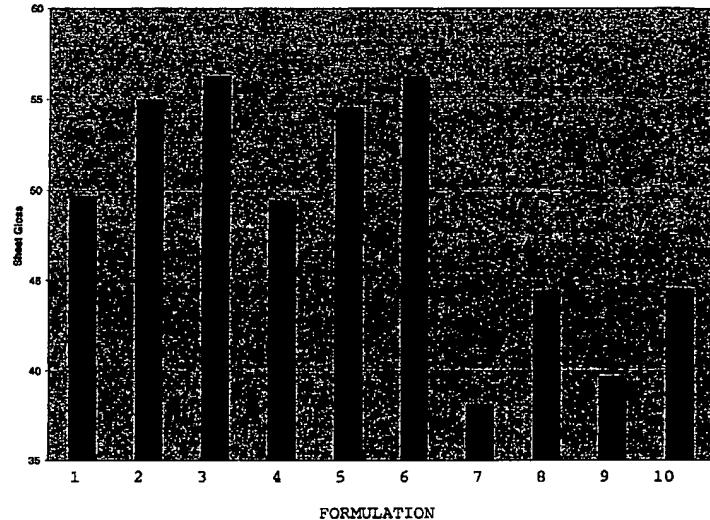
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(71) Applicant (for all designated States except US): DOW GLOBAL TECHNOLOGIES INC. [US/US]; Washington Street, 1790 Building, Midland, MI 48674 (US).

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: COATING AND FILLER COMPOSITIONS COMPRISING PLATY LAYERED SILICATE PIGMENTS



WO 2004/101691 A3

(57) Abstract: A coating composition comprising platy magadiite pigment(s); a paper product comprising platy magadiite pigments; and an aqueous suspension comprising platy magadiite and a suspending agent selected from the group consisting of ;polyacrylate polymers, polyvinylalcohol polymers, maleic anhydride-containing copolymers, and polyphosphates, and a latex dispersion or emulsion of latex polymers selected from the group consisting of styrene butadiene polymers, acrylic polymers, carboxylated acrylonitrile :butadiene polymers, polyvinylchloride, polyvinylidenechloride, polystyrene, fluorinated polyethylene and polypropylene, and polytetrafluoroethylene; and an article or formulation comprising a platy layered silicate.



**Published:**

— *with international search report*

(88) **Date of publication of the international search report:**

6 May 2005

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/013044

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7	C09C1/00	C09D7/12	C09D5/00	C09D11/02	C08K3/34
	C08K7/00	D21H17/68	D21H19/40		

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09C C09D C08K D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/055580 A1 (LORAH DENNIS PAUL ET AL) 9 May 2002 (2002-05-09) paragraphs [0001], [0023], [0033], [0042], [0046], [0106] - [0110] -----	1,2,6-8
X	WO 98/56861 A (MICHELIN RECH TECH ; HERBERTS GMBH (DE); WARD BENNETT C (DE); GOLDBERG) 17 December 1998 (1998-12-17) page 1 - page 2 page 9 - page 10 -----	1,2,6,8
X	WO 97/31057 A (DOW CHEMICAL CO) 28 August 1997 (1997-08-28) pages 1,3,6,8 page 14 ----- -/-	1,6-8

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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Date of the actual completion of the international search

29 October 2004

Date of mailing of the International search report

21.02.05

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/U52004/013044

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98/29491 A (WHITE JERRY E ; CHOU CHAI JING (US); DOW CHEMICAL CO (US); ANDERSON KE) 9 July 1998 (1998-07-09) pages 1,6-10 -----	1,6,8

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US2004/013044

### Box II Observations where certain claims were found unsearchable (Continuation of Item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
  
3.  Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box III Observations where unity of invention is lacking (Continuation of Item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-8

#### Remark on Protest

The additional search fees were accompanied by the applicant's protest.  
 No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-8

a coating composition comprising platy layered silicate pigment(s)

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2. claims: 9-12

a paper product comprising platy layered silicate pigments

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3. claims: 13,14

a latex product comprising platy layered silicate pigments

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4. claim: 15

a cardboard product comprising platy layered silicate pigments

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5. claim: 16

paints or films for road signs comprising platy layered silicate pigments

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6. claim: 17

ink products comprising platy layered silicate pigments

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7. claim: 18

a flame retardant composition comprising platy layered silicate pigments

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8. claims: 19-27

a comprising platy layered silicate, a suspending agent and either a latex polymer or a binder

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9. claims: 28-31

an article or formulation selected from (1) a nanofiller in polyolefin nanocomposites, (2) a paint pigment formulation or (3) a catalyst support for polyolefin catalysts, each comprising a platy layered silicate

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/U52004/013044

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002055580	A1 09-05-2002	AU 8911801 A AU 8911901 A AU 9102401 A AU 9102501 A AU 9102601 A BR 0113995 A BR 0113997 A BR 0113998 A BR 0113999 A BR 0114000 A BR 0114001 A CN 1461314 T CN 1462281 T CN 1462282 T CN 1462283 T CN 1462280 T EP 1328554 A2 EP 1328555 A2 EP 1322675 A2 EP 1325037 A2 EP 1325038 A2 EP 1328553 A2 JP 2004509983 T JP 2004509984 T JP 2004509985 T JP 2004509986 T JP 2004509987 T JP 2004517980 T TW 570942 B TW 575612 B TW 584638 B TW 587083 B WO 0224756 A2 WO 0224757 A2 WO 0224758 A2 WO 0224759 A2 WO 02055563 A2 WO 0224760 A2 US 2004054068 A1 US 2004220317 A1 US 2002058739 A1 US 2002055581 A1 US 2002086908 A1 US 2002058740 A1 US 2002055599 A1	02-04-2002 02-04-2002 02-04-2002 02-04-2002 02-04-2002 12-08-2003 05-08-2003 12-08-2003 12-08-2003 12-08-2003 19-08-2003 10-12-2003 17-12-2003 17-12-2003 17-12-2003 17-12-2003 23-07-2003 23-07-2003 02-07-2003 09-07-2003 09-07-2003 23-07-2003 02-04-2004 02-04-2004 02-04-2004 02-04-2004 02-04-2004 17-06-2004 11-01-2004 11-02-2004 21-04-2004 11-05-2004 28-03-2002 28-03-2002 28-03-2002 28-03-2002 18-07-2002 28-03-2002 18-03-2004 04-11-2004 16-05-2002 09-05-2002 04-07-2002 16-05-2002 09-05-2002
WO 9856861	A 17-12-1998	AU 7837198 A WO 9856861 A1	30-12-1998 17-12-1998
WO 9731057	A 28-08-1997	AU 2132097 A BR 9707663 A CA 2247148 A1 CN 1214711 A EP 0882092 A1 JP 2000505490 T WO 9731057 A1	10-09-1997 13-04-1999 28-08-1997 21-04-1999 09-12-1998 09-05-2000 28-08-1997
WO 9829491	A 09-07-1998	BR 9707876 A	27-07-1999

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/US2004/013044

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9829491	A	CA 2246269 A1	09-07-1998
		CN 1212716 A	31-03-1999
		CZ 9802735 A3	13-01-1999
		EP 0889931 A1	13-01-1999
		ID 23684 A	11-05-2000
		JP 2000508021 T	27-06-2000
		NO 983965 A	28-10-1998
		PL 328862 A1	01-03-1999
		WO 9829491 A1	09-07-1998
		US 6156835 A	05-12-2000

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